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KRONIG-PENNEY MODEL OF A SEMICONDUCTING COMPOUND

Dr. B. Seraphin (Siemens-Schuckertwerke, Erlangen) has developed a simple one-dimensional Kronig-Penney model of a semiconducting compound, which explains many of the properties of InSb-type compounds in a semi-quantitative manner. This model is a considerable improvement over the one reported by Seraphin and H. Welker at the Innsbruck meeting of the German Physical Society last September (see Technical Report ONRL-131-53). In the present model, the zincblende lattice structure is taken into account in the following way: the direction of propagation of all electron waves is taken perpendicular to the close-packed planes in the lattice, and the positions of these planes are denoted by potential wells (see Fig. 1).

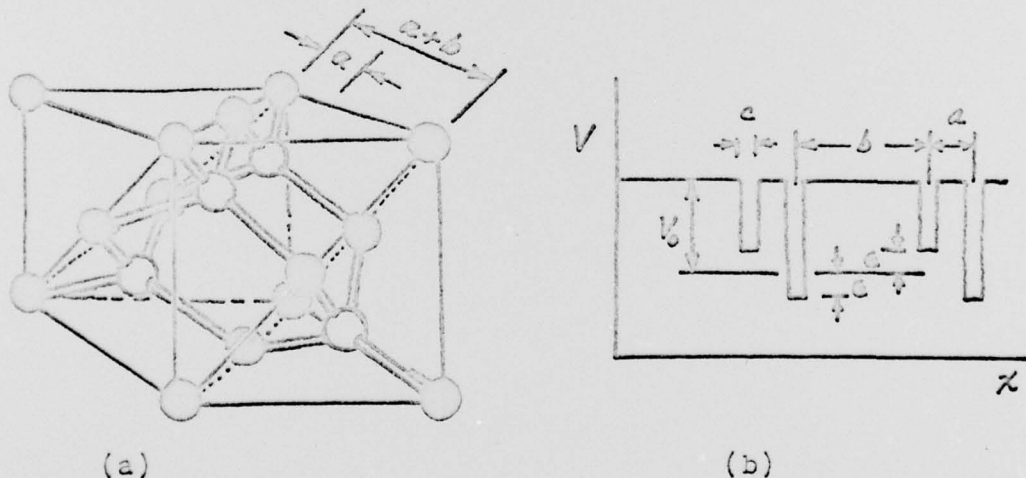


Fig. 1. Kronig-Penney Model of a Semiconductor with Zincblende Structure.

The ratio of distances between consecutive planes, i.e., b/a , is three for the zincblende structure.

The two kinds of atoms in the zincblende structure are represented by two different potential wells of depth $V_0 + \epsilon$ and $V_0 - \epsilon$. The transition to the Kronig-Penney parameter, P , is made in the usual way:

$$P = \lim 4\pi^2 mc(a+b)V_0/h^2,$$

$$\Delta P = \lim 4\pi^2 mc(a+b)\epsilon/h^2,$$

where c is the width of the potential well. The calculated band structure as a function of ΔP is shown in Fig. 2 for the case where $P = 3$.

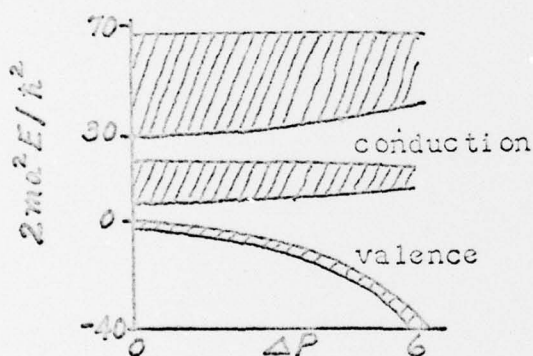


Fig. 2. Band Structure of a One-Dimensional Semiconducting Compound. ($P=3$) Energy, E , v.s. ΔP

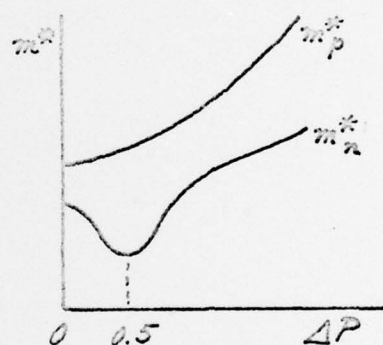


Fig. 3. Effective Mass of Electrons and Holes for a Semiconducting Compound. $P=3$

Since the effective mass, m^* , of the charge carriers is proportional to $(\partial^2 E / \partial k^2)^{-1}$, the effective masses of electrons and holes were determined by Seraphin from the

$$\cos [k(a+b)] = F(E, P, \Delta P)$$

relationship at the bottom of the conduction band and the top of the valence band. The results are shown as a

function of ΔP in Fig. 3. It was then possible to obtain the mobilities of electrons and holes from the relationship:

$$\mu \propto (m^*)^{-5/2}.$$

Seraphin's model seems to explain all of the basic properties of semiconducting compounds of the $Al^{III}BV$ -type, such as GaAs, in relation to the properties of semiconducting Group IV elements, such as Ge. The model explains the increase in electron mobility and the decrease in hole mobility in the compounds, the increase in the width of the forbidden zone, and the increase in melting point (due to the increased binding in the valence band). A detailed account of this work will appear in *Zeitschrift für Naturforschung*.

SLIP PLANE OF A DISLOCATION JOG

Dr. A. Seeger (Technical University, Stuttgart) has recently made a general theoretical analysis of the slip plane and direction of a dislocation jog. He considers the jog produced in a dislocation line 1, when this dislocation with Burgers vector \underline{b}_1 and slip plane E_1 cuts through the dislocation line 2 (with Burgers vector \underline{b}_2) not lying in the slip plane E_1 . The results of Seeger's investigation can be formulated as follows: the slip plane of the jog in the dislocation 1 is the plane defined by \underline{b}_1 and \underline{b}_2 ; the direction and length of the dislocation line in the jog are given, in the case where neither dislocation 1 nor 2 are dissociated into partial dislocations and where no additional external forces are acting, by the direction and magnitude of the projection of \underline{b}_2 on the rectifying plane of dislocation 1 at the point of intersection of the two dislocations. This rectifying plane is defined by the normal to slip plane E_1 and the tangent to dislocation line 1.

There is one exceptional case which must be discussed separately; this is the case where dislocation 1 is a pure screw dislocation before it crosses 2. The slip plane of the jog is still defined by \underline{b}_1 and \underline{b}_2 , but no general statement can be made about the length of the jog. The reason for this is that a screw dislocation has infinitely many slip planes and therefore infinitely many rectifying planes. Which slip movements of the dislocations are produced during and after jog formation depend in this

case mainly upon which slip planes are energetically favored in the crystal structure.

An account of this work will appear in Zeitschrift für Naturforschung.

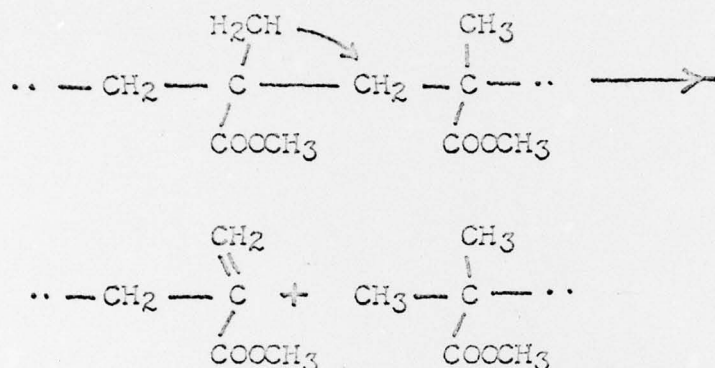
THE EFFECT OF IONIZING RADIATION ON HIGH POLYMERS

Work in progress in the Division of Metallurgy of the Atomic Energy Research Establishment at Harwell on the effect of ionizing radiation on high polymers continues to yield interesting results. Dr. A. Charlesby and his collaborators have investigated the effect of ionizing radiations in the pile on a variety of high polymers and made detailed studies on the behavior of polyethylene and of polymethylmethacrylate.

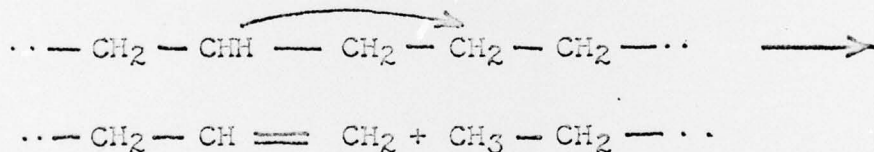
Macromolecules in the solid state undergo either cross-linking or chain breakdown when subjected to ionizing radiation. The experimental data available indicate that chain breakdown occurs in Teflon (polytetrafluoroethylene), polyisobutylene and polymethylmethacrylate. The other polymers investigated, such as polyethylene, polyvinyl alcohol, polystyrene and rubber, undergo cross-linking resulting in the formation of an insoluble gel. Both processes are accompanied by the evolution of gaseous products. The experimental techniques used by Charlesby's group are generally simple ones and they have obtained a considerable amount of valuable information from solubility and viscosity data. The macroscopic behavior of the individual polymer systems is different even when the basic effect is the same, i.e., cross-linking or degradation. The three polymers in which degradation was observed each show a typical behavior. Upon extensive irradiation Teflon decomposes to a fine powder, polyisobutylene becomes a viscous liquid whose molecules consist of 10 - 15 monomers, and polymethylmethacrylate becomes a milky-looking solid which, when heated above the softening point "blows up" into a very light dry sponge. This striking effect is due to the coagulation of the finely dispersed gas molecules or clusters of molecules into larger bubbles and their subsequent expansion.

In collaboration with M. Ross (Harwell) and P. Alexander (London) the degradation of solid polymethylmethacrylate was investigated in some detail, and Dr. Charlesby discussed this work at a recent meeting of the

Royal Society in London. The changes in molecular weight were followed by viscosity measurement and they are consistent with the assumption that main-chain fracture occurs at random and is proportional to the dosage. A mechanism was proposed, according to which the main-chain breaks are accompanied by chemical rearrangement to give two stable entities which do not combine. This involves the migration of a hydrogen atom as is shown by the following scheme:



Polyisobutylene presumably behaves in a similar manner. On the other hand, the analogous process in polyethylene



would require that the hydrogen atom "jump" one carbon atom, and model considerations suggest that this is unlikely. Thus cross-linking may be expected here and this had of course been observed some time ago.

It was found that the amount of degradation can be reduced by the addition of small amounts of foreign substances. Among these, benzoquinone gave 70% protection, aniline 64.2%, phenol 64.2%, α -naphthylamine 60.6%, ethylurea 17.5%, while paraffin has no effect whatever. It was suggested that this protective effect involved an energy transfer process by which the protective molecules relieve the polymer of its excess energy before this has led to dissociation.

KINETICS AND MECHANISM OF INORGANIC REACTIONS IN SOLUTION

The kinetics and mechanism of inorganic reactions in solution were surveyed at a Discussion of the Chemical Society held in London on February 4. The meeting consisted of seven prepared lectures, followed by discussion. The main topic of interest was electron transfer processes, while complexes, octahedral substitution, and disproportionation reactions of transuranic elements were among the other subjects discussed. It is planned to publish in full the papers and discussion as a special publication. A few of the noteworthy new results presented from British universities are briefly described below, while a somewhat more detailed account of the meeting is given in Technical Report ONRL-20-54.

Nickel Complexes

In his introduction to the Discussion Dr. H.M.N.H. Irving (Oxford) surveyed the difficulties of reaction mechanism problems in inorganic chemistry. He also described some of the work in progress on the heat of complexing of Ni^{2+} with ethylenediamine and some of its methyl derivatives. A sensitive differential calorimetric technique permits conclusions to be drawn regarding the relative speed of some of the processes which occur. It was mentioned that in general the rate of complexing with the first and with the second ligand is considerably faster than with the third one.

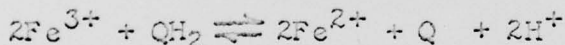
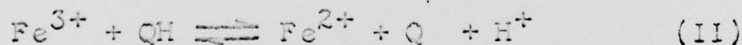
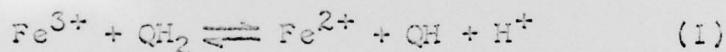
Octahedral Substitution

Prof. C. K. Ingold summarized the extensive investigations carried out at University College on the mechanism and stereochemistry of octahedral substitution. The displacement of chlorine from 1-cis-dichlorobisethylenediaminecobalt-III by a graded series of nucleophilic agents revealed that these fall into two different groups. Methoxy, azide, and nitrite undergo second order reactions with a variation in rate by a factor of 30,000. The other four nucleophilic agents investigated, thiocyanate, hydroxyl, chloride and nitrate react with first order kinetics and at an essentially identical rate. The first order, S_N1 reaction is interpreted in terms of an intermediate of low concentration being formed in a slow reaction which in turn reacts rapidly with the nucleophilic agent in question. This intermediate is optically inactive and must possess either a triangular-bipyramid or a square pyramid structure.

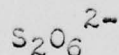
The second order S_N2 substitution involves about 75 per cent change in optical activity and is best described as an "edge-displacement". It is important to keep in mind, as can be shown by consideration of models, that such an edge displacement process is quite different stereochemically from inversion on a tetrahedral carbon atom. In particular, it can be misleading to call its consequence a cis-trans or optical inversion without carefully specifying the stereochemical reference point used in the octahedral system.

Electron Transfer Processes

Interesting new results were presented on electron transfer processes from the University of Manchester. Dr. J. H. Baxendale discussed the mechanism and kinetics of the reactions of the ferric-ferrous system with thallic-thalious, and with some quinone-hydroquinone systems. The results obtained with these latter systems strongly suggest a true electron transfer reaction. The kinetics of these reactions are consistent with the reaction occurring through a reversible one-electron step involving the formation of an intermediate of abnormal valency, followed by a second-electron step, according to the following general scheme:



According to recent results obtained by Dr. W.C.E. Higginson the oxidation of the sulfite ion may provide an interesting analogy to that of hydrazine as regards the behavior of different types of oxidizing agents. Again, in accordance with previous investigators, two different reaction paths are recognized, namely, oxidation to sulfate and dimerization to dithionate,



The two-electron acceptor oxidants, Ti^{3+} , IO_3^- , Br_2 , and I_2 produce only sulfate while the one-electron oxidants,

Ce^{4+} , Ce^{3+} and Fe^{3+} yield a mixture of sulfate and dithionate of varying proportions depending on the concentration.

The recent observation that the reaction between thallic ions and mercurous ions is very much faster than the action of other, much stronger oxidizing agents on the mercurous ion, may provide an interesting case of two-electron transfer. Dr. Higginson suggested that the Hg-Hg bond does not have to be broken in this case but that the Hg_2^{++} accepts two electrons in a single step.

A SIMPLE MICROCALORIMETER

Dr. E. W. Clarke of the Royal Air Force Institute of Aviation Medicine, Farnborough, has developed an apparatus to measure the aerobic and anerobic heat production of several different types of biological material. The principle of the method is to determine the steady flow of heat from a test chamber by measuring the temperature difference across its walls. The temperature of the inside of the wall is not compared directly with the outside but with a similar compensating chamber which contains no source of heat.

The calorimeter consists of two thin-walled glass chambers, of approximately 2 cc capacity, arranged end to end and separated by an insulating partition. Surrounding the cylindrical surface of the two chambers is a thermopile. The 'cold' junctions of the thermopile are evenly distributed over the surface of one chamber and the 'hot' junctions similarly arranged over the surface of the other chamber. Approximately 150 copper-constantan couples are used and have a resistance of 50 ohms. The whole unit is placed inside a thick glass tube and the space between the chambers and the tube filled with a compound wax. The thermopile leads are taken away through a glass supporting tube. The chambers are closed with rubber stoppers and one of them is fitted with a small heating coil used for calibration. Each stopper admits two fine stainless steel delivery tubes for introducing gases and liquids into the chambers. The apparatus is placed in an accurately thermostated water-bath and the thermopile connected to an ordinary low-resistance galvanometer.

The galvanometer deflection was found to be directly proportional to the heat liberated in the test chamber, a fact which greatly simplifies calibration and permits the use of direct galvanometer readings. When

measuring low rates of heat production the chambers must be completely filled by the liquid in order to minimize heat fluctuation by evaporation. The compensating chamber is filled with a substance of similar heat capacity to the material in the test chamber to equalize, as far as possible, the heat flows caused by temperature fluctuation of the water-bath.

A double-jacket water-bath is used. The outer jacket is provided with a stirrer, heater and mercury-toluene regulator. The inner jacket consists of a completely closed copper box and contains the calorimeter and a small constant-speed stirrer. The inconstancies of the water-bath have so far been the main factor limiting the accuracy of the method for low heat-rate determinations. With the present bath the apparatus has a zero fluctuation equivalent to ± 0.001 cal/hr.

THE EFFECT OF DIETARY CALCIUM LEVEL ON BONE ABSORPTION DURING PREGNANCY AND LACTATION

J. Duckworth and R. Hill of the Rowett Research Institute, Aberdeen, have been conducting experiments on the effect of the level of dietary calcium during pregnancy and lactation on the skeleton of the ewe. Three groups of ewes (12 per group) were given the same diet but different amounts of calcium supplement throughout pregnancy and lactation periods. Group 1 received 1.4 g calcium daily; Group 2, 4.5 g; and Group 3, 7.4 g. Resorption of bone was measured at the end of lactation by two methods, X-ray examination and determination of total ash of bones taken from all parts of the body. Using total ash of the skeleton as a measure, a statistically significant difference (19 per cent) was found between Group 1 and Group 3. The difference (5 per cent) between Groups 2 and 3 was not statistically significant. Some parts of the skeleton were affected more severely than others; in order of decreasing amount of resorption the parts of the skeleton may be listed as follows: vertebrae; pelvis; skull; sacrum; mandible; ribs; proximal end of tibia; scapula; sternum; ends of humerus, radius and femur; distal end of tibia; shafts of humerus, radius, femur and tibia; metacarpal; metatarsal. The level of calcium intake did not affect reproductive performance, lactation, or survival of lambs.

MUTATIONS IN S. CEREVISIAE

Prof. J. Maisin, the Cancer Institute, University of Louvain, is conducting a study of mutations in

Saccharomyces cerevisiae produced by adding methyl cholanthrene to the medium. It was found that when the normal white colonies grown on glucose-peptone agar in the presence of carbowax are exposed to methyl cholanthrene, rose-colored mutants are produced. In an effort to cause a reversion of the rose mutants to the normal white colonies, it has been determined that the change may be brought about in one of three ways: the amount of glucose in the medium may be reduced, the subculture may be exposed to ionizing radiations and, most recently, it has been found that an extract of the white colonies produced by a modified Chargoff technique, when added to the culture of rose mutants, causes a reversion to the white colonies. Work is now in progress to determine the chemical composition and mechanism of action of the cellular extract.

THE CORRELATION BETWEEN HISTOLOGICAL AND RADIOLOGICAL APPEARANCES IN INJECTED BRONCHI

Dr. Lynn Reid of the Brompton Hospital, London, has devised an apparatus for preparing lungs for complete radiological examination. It consists of a lucite box which is connected with a vacuum pump and in which a whole lung or pair of lungs may be placed in such a manner that the bronchi can be connected with an in-flow tube. The lungs are inflated by starting the vacuum pump and allowing atmospheric air to pass into the in-flow tube. When the desired expansion is achieved, the in-flow tube is connected with a reservoir which contains a mixture of red lead (50 per cent by weight) in liquid gelatin. This mixture is allowed to fill the lungs at a pressure of 5 pounds per square inch. The lungs are then fixed and selected portions of the secondary lobules in areas presumed, after examination of the bronchogram, to be diseased are serially sectioned. The absence of the peripheral bronchiolar pattern in a bronchogram with a tapering or bulbous termination of the secondary bronchi or bronchioles indicates obstructive diseases of the tubes. Where the terminations of the secondary bronchi or bronchioles appear in the bronchogram to have parallel sides and a square end, the obstruction is due to the presence of a mucous plug. It is found that the bronchographic picture in diseases such as emphysema, chronic bronchitis, bronchiectasis and certain tuberculous infections can definitely be correlated with the histologic picture.

PERSONAL NEWS ITEMS

Prof. D. M. Everett (Dundee) has been elected to the Chair of Physical and Inorganic Chemistry at Bristol University. He is to succeed Prof. W. E. Garner, F.R.S., who retires at the end of the current academic year.

Prof. A. Flammersfeld of the Max-Planck Institut für Chemie, Mainz, has recently been appointed Director of the Second Physical Institute at the University of Göttingen. He will assume his new duties shortly.

R. Fleischmann, formerly professor of physics at the University of Hamburg, is now Director of the Physical Institute at the University of Erlangen.

Prof. A. H. Cottrell of the Metallurgy Department, University of Birmingham, has been awarded the 1954 Rosenhain Medal by the Institute of Metals in recognition of his outstanding contributions to the field of physical metallurgy.

NEW GERMAN JOURNAL OF PHYSICS

A new journal of physics entitled Fortschritte der Physik is being published by the Akademie-Verlag, Berlin, N.W.7. It is edited by Prof. F. Möglich of the Humboldt University in East Berlin. The articles appearing in this journal are of a review nature; about half of them are original articles by authors in West and East Germany, a few by authors in Soviet satellite countries, and the remainder are German translations of the best Russian papers in Uspekhi Fizicheskikh Nauk (Progress of Physical Science). Articles by W. L. Ginsburg, S. I. Pekar, and L. Infeld appeared in Volume 1.

The journal is available through bookstores in Western Germany at DM. 5 per issue; there are approximately twelve issues per volume. The first volume of the journal appeared in 1953.

TECHNICAL REPORTS OF CNRL

The following reports have been forwarded to CNR, Washington. Copies may be obtained by addressing requests to the Commanding Officer, Office of Naval Research Branch Office, Navy No. 100, c/o Fleet Post Office, New York, N. Y.

- ONRL-13-54 "Scientific Research in Yugoslavia" by
G. J. Szasz
- ONRL-14-54 "The Institute of Nuclear Sciences 'Boris
Kidrich' in Vincha-Belgrade, Yugoslavia"
by G. J. Szasz
- ONRL-17-54 "The Eight-Eight Meeting of the Pathological
Society of Great Britain and Ireland" by
J. L. Tullis
- ONRL-18-54 "Mutations Induced in Lower Forms of Life
by Ultra-Violet Rays and Chemical Substances"
by J. L. Tullis
- ONRL-19-54 "Some Current Research in the Department of
Pathology of the University of Birmingham"
by J. L. Tullis

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